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The Theoretical Evaluation of the Possibility of the CoO(OH)-Assisted Paraquat Electrochemical Detection

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Abstract

The possibility of use of cobalt (III) oxyhydroxide as an electrode modifier in electrochemical analysis of paraquat pesticide has been evaluated from the theoretical point of view. The electrochemical function mechanism has been suggested, and the correspondent mathematical model has been analyzed by means of linear stability theory and bifurcation analysis. It was shown that the cobalt (III)oxyhydroxide may be efficient cathode modifier for paraquat electrochemical reduction in neutral media. The steady-state stability is maintained in vast parameter region. The possibility for oscillatory and monotonic instabilities has also been verified.

Keywords: *food security, intoxication prevention, paraquat, electrochemical sensors, cobalt (III)oxyhydroxide, stable steady-state*

Introduction

The use of chemically modified electrodes [1 – 7] provides the possibility of flexible electrochemical analysis of different substances. Its advantages are precision, exactitude, rapidity and sensibility of the analysis and also the electrode affinity to the analyte.

One of the materials, possible used as an electrode modifier for electroanalytical systems is cobalt (III) oxyhydroxide [8 – 10]. Seen as an alternative to titanium dioxide, it is a p-type semiconductor

with possible use in photo-, photoelectro- and electrocatalytical systems. Nevertheless, its electroanalytical use investigation has only begun in the present decade [11 – 12], so, its use in sensors requires special care.

On the other hand, paraquat is one of the most efficient non-selective herbicides in the world [13 – 15], killing green plants on contact. It is used not only as a herbicide, but also a simulation substance for oxidation stress. Nevertheless, even being a strong herbicide, it is also extremely toxic for human organism [16 – 19], and also for other mammals [20]. The high toxicity of the compound even made it used to assist suicides and murders [21 – 22], and its prohibition in South Korea contributed strongly on the suicide rate and profile in the country [21]. Moreover, there is no specific antidote for paraquat. So, the development the development of an exact, precise, sensitive and rapid method of its detection is really an actual problem – not only for intoxication prevention, but also for intelligence and criminal investigation [22 – 26].

In the work [26], a novel methodology for paraquat electrochemical detection, based on NiO-modified cathode, has been used. Although CoO(OH) hasn't been used as an electrode modifier in paraquat electroanalysis yet, it is possible to predict that the use of CoO(OH) may be viable in this case.

Nevertheless, the possible application of cobalt (III) oxyhydroxide as a cathode modifier in paraquat electrochemical detection may confront problems like:

- the incertainity concerning the mechanism of CoO(OH) electroanalytical mechanism with paraquat;

- the possibility of electrochemical instabilities, capable to accompany either the CoO(OH) electrochemical synthesis [27 – 28],or paraquat electrochemical reduction [26] (Fig. 1).
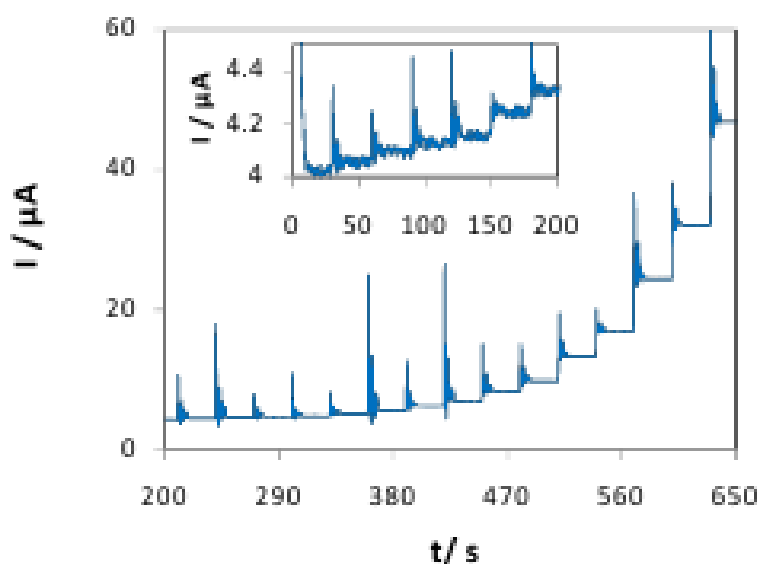

Fig. 1. Current oscillations, observed during paraquat electrochemical detection over nickel compounds, accompanied by its successive adition. Reproduced from [26] with permission of Centre of Excellence in Electrochemistry, University of Tehran, Islamic Republic of Iran

The resolution of both problems can't be realized without the development of a mathematical model, capable to describe adequately the processes in this system.

So, the general aim of this work is the mechanistic theoretical evaluation of the possibility of CoO(OH)-assisted paraquat electrochemical reduction for electroanalytical purposes. Its realization requires the achievement of specific goals like:

- The suggestion of the reaction mechanism, including CoO(OH) function in the process;

- Development of the mathematical bodel, based on this mechanism;

- The steady-state stability analysis of this system (based on the model);

- Verification of the possibility of electrochemical instabilities realization in it;

- Comparison of its behavior with that of the similar systems [29 - 32].

System And Its Modeling

Taking in account the CoO(OH) chemical and electrochemical properties, like also paraquat electrochemical reduction kinetics, the mechanism of the sensor may be suggested as:

$$CoO(OH) + e^- \rightarrow CoO + OH^- \qquad (1)$$

 $+ 2CoO + 2OH^- \rightarrow$ $+ 2CoO(OH)$ (2)
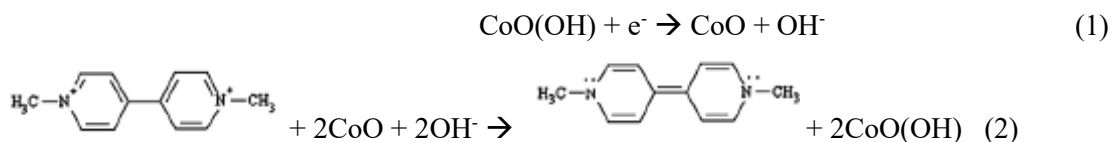
As the trivalent state for cobalt is more stable than for niquel, the reaction (2) occurs more quickly than for the analogous case described in [26]. Nevertheless, with the cathodic potential applied, it will result on the concurrence between electrochemical reduction and formation of CoO(OH), influencing the system as described lower.

Taking into account the described above, to describe the system's behavior, we introduce two vatiables:

c – paraquat concentration in the pre-surface layer;

θ – CoO(OH) coverage degree on cathode.

To simplify the modeling, we suppose that the reactor is intensively stirred, so we may neglect the convection flow. Also we suppose that the supporting electrolyte is in excess, so we may neglect the migration flow. Also we suppose that the concentrational distribution on pre-surface layer is linear, and the layer thickness is constant, equal to δ.

It is possible to show that, in this case, the system may be described by next differential equation set (DES):

$$\begin{cases} \dfrac{dc}{dt} = \dfrac{2}{\delta}\left(\dfrac{\Delta}{\delta}(c_0 - c) - r_2 \right) \\ \dfrac{d\theta}{dt} = \dfrac{1}{G}(r_2 - r_1) \end{cases} \qquad (3),$$

in which c_0 is the paraquat bulk concentration, Δ, is its diffusion coefficient, G is CoO(OH) maximal concentration on the cathode surface, and r_1 and r_2 are correspondent reaction rates, which may be calculated as:

$$r_2 = k_1 c (1-\theta)^2 \tag{4}$$

$$r_1 = k_2 \theta \exp\left(-\frac{F\phi_0}{RT}\right) \tag{5},$$

in which the parameters k are respective rate constants, F is the Faraday number, ϕ_0 is the DEL potential slope, correspondent to the zero-charge potential, R is the universal gas constant and T is absolute temperature. The potential slope is dependent on θ according to the relation $\phi_0 = \gamma\theta$.

A classical DES is obtained. It has been observed for conducting polymers [29] and ferrocene [30]. Nevertheless, its applicability to the present system has some restrictions and observations, which may be described lower.

Results And Discussion

In order to investigate the behavior of the system with paraquat electrochemical detection over CoO(OH), we analyze the DES (3) by means of linear stability theory. The steady-state Jacobian functional matrix for this system will be described as:

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \tag{6},$$

in which

$$a_{11} = \frac{2}{\delta}\left(-\frac{\Delta}{\delta} - k_1(1-\theta)^2\right) \tag{7}$$

$$a_{12} = \frac{4}{\delta}\left(k_1 c (1-\theta)\right) \tag{8}$$

$$a_{21} = \frac{1}{G}\left(k_1(1-\theta)^2\right) \tag{9}$$

$$a_{22} = \frac{1}{G}\left(-2k_1 c(1-\theta) - k_2 \exp\left(-\frac{F\phi_0}{RT}\right) + \gamma k_2 \theta \exp\left(-\frac{F\phi_0}{RT}\right)\right) \tag{10}$$

Taking into account the matrix elements (7) and (10), it is possible to see that the unique positive element, responsible for the positive callback and, consequently, for the *oscillatory behavior* in this system is $\gamma k_2 \theta \exp\left(-\frac{F\phi_0}{RT}\right)$. The principal condition of Hopf-Andronov bifurcation, describing this type of behavior, is Tr J = 0, in which Tr J = $a_{11} + a_{22}$, and the oscillatory behavior will be realized if the condition of:

$$\frac{1}{G}\gamma k_2\theta\exp\left(-\frac{F\phi_0}{RT}\right) = \frac{1}{G}\left(2k_1c(1-\theta) + k_2\exp\left(-\frac{F\phi_0}{RT}\right)\right) + \frac{2}{\delta}\left(\frac{\Delta}{\delta} + k_1(1-\theta)^2\right) \qquad (11)$$

is satisfied. This condition may only be realized with positive γ values, describing strong DEL influences of the electrochemical reaction, causing the oscillations, analogous to those observed in [26]. Nevertheless, as in this case the trivalent state for cobalt is more stable, than for niquel, in this system the effect, produced by electrochemical reduction, concurs with CoO(OH) formation, and the oscillations will be different – more frequent and of less amplitude.

The *steady-state stability* conditions in bidimensial systems is Tr J<0, Det J>0, in which Det J = $a_{11}a_{22} - a_{21}a_{12}$. To avoid the appearance of cumbersome expressions, we introduce new variables, for the Jacobian determinant to be described as:

$$\frac{2}{\delta G}\begin{vmatrix} -\kappa - \Xi & \Omega \\ \Xi & -\Omega - \Lambda \end{vmatrix} \qquad (12)$$

Opening the brackets, we obtain the steady-state stability condition, described as:

$$\kappa\Lambda + \Xi\Lambda + \kappa\Omega > 0 \qquad (13)$$

This condition is satisfied with warranty, if Λ is positive, which is defining the absence or fragility of DEL influences of electrochemical reaction. The stability is realized in a vast parameter region. From the electroanalytical point of view it is correspondent to the linear dependence between cathodic current and paraquat concentration, so it is possible to confirm that the process will be electroanalytically efficient.

When the paraquat concentrations are relatively small, the diffusion is kinetically the slowest process, and the electroanalytical process will be diffusion controlled. Yet, when the paraquat concentration values are higher, the reaction (2) will be, kinetically, slower than the diffusion, and this reaction will control the electroanalytical process.

In the case of the equality of destabilizing and stabilizing influences of electrochemical reaction, the *monotonic instability,* correspondent to the detection limit, is realized, and its condition for this system will be presented as:

$$\Lambda = -\frac{\kappa\Omega}{(\kappa + \Xi)} \qquad (14)$$

The inclusion of other analytical signals. In this system, it is possible to use the pH change as an analytical signal. As the reaction (2) may only be realized with paraquat, present in the solution, only the reaction (1) is realized when paraquat is completely transformed, and the pH value increases. So, the pH-measure is one more important electroanalytical factor to be used during paraquat electrochemical reduction on CoO(OH).

Conclusions

The mechanistic theoretical evaluation of CoO(OH)-assisted paraquat electroanalysis let us conclude that:

- the oscillatory behavior in this case is possible and may be influenced only by influences of the electrochemical reaction on double electric layer;

- although it is the unique factor, responsible for the oscillatory behavior, in the system with CoO(OH) it is manifested by different manner, that for the case of nickel compounds, because of the enhanced stability of the trivalent state of cobalt, compared to that of niquel. The oscillations have to be more frequent and of smaller amplitude, than for the case of niquel;

- the steady-state stability is warranted by the absence or fragility of DEL influences of electrochemical reactions in double electric layer. It is maintained in a vast parameter region;

- with small paraquat concentrations, the process is diffusion-controlled, and with greater concentrations, it is reaction controlled;

- in the case of the equality of destabilizing and stabilizing influences, the monotonic instability, correspondent to the detection limit, is realized;

- to make the process more electroanalytically efficient, it is possible to use the electrochemical process, coupled with pH-measuring.

Conflict of interest

The authors declare that there is no conflict of interests regarding this publication

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